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<b>(21) International Application Number:</b> PCT/US89/05261 <b>(22) International Filing Date:</b> 28 November 1989 (28.11.89)  <b>(30) Priority data:</b> 278,913 2 December 1988 (02.12.88) US 288,577 22 December 1988 (22.12.88) US 426,916 24 October 1989 (24.10.89) US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventor:</b> HOWARD, Edward, George, Jr. ; 844 Old Public Road, Hockessin, DE 19707 (US).  <b>(74) Agents:</b> FISHER, Lynn, N. et al. ; E.I. du Pont de Nemours and Company, Legal Department, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), BR, CH (European patent), DE (European patent), DK, ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), SU.  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE, ARTICLES AND PROCESSES OF MANUFACTURE  <b>(57) Abstract</b>  Novel ultrahigh molecular weight linear polyethylene (UHMWLPE) in the form of a shaped article, exhibiting a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body. A novel process for preparing this article is also disclosed.		

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TITLE

ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE,  
ARTICLES AND PROCESSES OF MANUFACTURE

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Serial No. 07/426,916 filed October 24, 1989 which in turn is a continuation-in-part of U.S.

Serial No. 07/288,577 filed December 22, 1988, which in turn is a continuation-in-part of U.S. Serial No. 07/278,913 filed December 2, 1988.

BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to a novel ultrahigh molecular weight linear polyethylene (UHMWLPE). This novel UHMWLPE, in the form of a shaped article, exhibits in various embodiments a unique combination of properties making the material useful as a bearing surface, in general, but particularly useful as a prosthetic hip joint cup and as other prosthetic shapes for replacement of other joints of the human body.

## 2. Description of the Prior Art

In U.S. Patent No. 3,944,536 (March 1976), Lupton et al describe UHMWPE in the form of a fabricated article exhibiting an elastic modulus of 340,000 to 500,000 psi, a tensile impact strength of 140 to 600 ft lb/in<sup>2</sup>, a density of 0.95 to 0.98 g/cc at 25°C, a crystalline melting point of 142 to 148°C (as measured by differential thermal analysis) and a unique crystalline form characterized by the absence of fold spacings of 50-2000 Angstrom units (Å) and the presence of crystal spacings of about 10,000 Å. The critical feature of the process of producing this UHMWPE is disclosed to involve inducing crystallization of the molten polymer above 150°C by

rapidly increasing the applied pressure from an initial level of 1 to 1000 atmospheres to a second level of 2000 to 7000 atmospheres and then cooling rapidly while maintaining a pressure sufficient to maintain the polyethylene in the solid phase until the temperature is below the crystalline melting point of the polyethylene at atmospheric pressure.

10 In Kunststoffe German Plastics 77 (1987) pp. 617-622, in an article entitled "Ultrahigh Molecular Polyethylene for Replacement Joints", Eyrer et al. point out that the service life of joint replacements made of UHMWPE is limited. Analysis of the damage to  
15 over 250 explanted hip cups and tibial plateaus revealed a changed property profile which they explained by post-crystallization resulting from oxidative chain decomposition. They suggested optimizing the processing of polyethylene under  
20 higher pressure and higher temperature to increase the degree of crystallinity. The Eyrer et al. product displays a creep of above 5% at a compression of 1000 psi (6.9 N/mm<sup>2</sup>) for 24 hours at 37°C.

One of the most remarkable advances in the  
25 medical field in recent years is the development of prosthetic joints, particularly the load bearing hip. The crippled and sometimes bed ridden elderly can walk again. The key to this development is UHMWPE because, not only does it have the necessary  
30 impact strength, but it initiates no adverse blood reactions. But at present, these prosthetic joints are limited to the older, less active segment of the population because the polymer tends to creep under the pressure that a younger more active person might  
35 develop while involved in recreation or employment. The creep would cause the loss of the close tolerance

required between the plastic socket and the polished metal ball attached to the femur. These changes in dimensions disturb the distribution of walking forces which in turn accelerates more creep and wear. Eventually the increased pain requires a traumatic revision operation. One objective of this invention is to provide UHMWPE prosthetic joints with improved creep resistance hence removing some of the age restriction existing on the present polyethylene joints.

#### SUMMARY OF THE INVENTION

The object of this invention is to provide a tough UHMWLPE composition and article with creep resistance that is less than 1% (as measured at a temperature of  $23 \pm 1^\circ\text{C}$  and a relative humidity of  $50 \pm 2\%$  for 24 hours under a comparison of 1000 psi) and that maintains excellent tensile and flexural properties.

Specifically, the product of this invention is a composition exhibiting an elastic or flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000 psi, a tensile modulus of 300,000-700,000 psi, preferably 300,000-600,000 psi, an elongation of 200-500%, a notched Izod impact resistance of 12-25 ft. lb. per in. of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of  $23^\circ\text{C}$  and a relative humidity of 50%, the polyethylene having a molecular weight of 1,000,000-10,000,000 (the molecular chain length between folds being greater than  $3500\text{\AA}$ ), a single crystalline melting point of greater than  $144^\circ\text{C}$  (as measured by differential scanning calorimetry) the reduction in said melting point upon reheating being

greater than 11°C above that of the starting polymer and an infrared crystallinity index of at least about 0.45, preferably at least 0.5. The composition may be formed into an article.

The process for obtaining the article of this invention involves six (6) important steps:

1. forming, by milling or casting or the like the article from UHMWLPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000 and most preferably at least 6,000,000;

2. placing the article in a pressure vessel (e.g. an autoclave) substantially filled with a fluid that is inert to the article, preferably water;

3. heating the vessel to a temperature of at least 190°C, preferably 200°C-230°C, and raising the pressure in the vessel, usually by adding additional water, to at least 2800 atmospheres (ATM), preferably at least 3000 ATM;

Alternately, the article, water, and reactor are heated to about 200-230°C, the pressure is applied and the system held at this temperature while polymer slowly loses heat of crystallization and solidifies.

Also, the pressure can be applied at any temperature during the heating cycle if the temperature exceeds about 200°C.

4. maintaining the temperature and pressure substantially as selected in step 3 for at least 0.5 hour, preferably at least one hour;

5. thereafter, cooling by reducing the temperature to a temperature at least below about 160°C-170°C preferably to 160°C or below, most preferably below 140°C, while maintaining a pressure of at least 2800 ATM preferably at least 3000 ATM, at a slow rate, the rate of cooling being such that

temperature gradients in the shaped article are substantially avoided. The polymer must be cooled slowly at the high pressure until it is fully crystallized. At 3000 ATM pressure, the crystallization temperature of UHMWLPE of over one million molecular weight is in the range of 170°C-190°C. The pressurized vessel should be cooled slowly to insure that the temperature of the polymer is not significantly above the vessel temperature, particularly if the pressure vessel construction does not permit means for measuring the temperature of the polymer itself.

6. cooling and releasing the pressure on the shaped article in a manner such that any remelting of the article is prevented. This is accomplished by cooling at least to a temperature below the atmospheric pressure melting point, i.e., about 130°C-135°C preferably below 120°C, most preferably below 100°C and releasing the pressure to reduce it from at least 2800 ATM to approximately 1 ATM, either sequentially or simultaneously. It should be understood that it is necessary to cool the polymer to a temperature below its melting point at any particular pressure to ensure that none of the polymer melts as the pressure is reduced since lowering the pressure lowers the melting point.

As an optional seventh step, it is advisable to shave the surface of the article, i.e. remove approximately the outer 2 millimeters that might contain any fluid-affected polymer.

A very important step is the fifth step, i.e. cooling in a manner that limits severe temperature gradients in the article. For example, for a 1 inch X 6 inch rod, a cooling rate of approximately 10°C

per hour is usually necessary. Although cooling rates no greater than 10°C per hour are preferred, cooling rates as high as about 35°C per hour have been used to provide the product of this invention. However, these latter rates require careful control in order to limit temperature gradients during cooling. Cooling rapidly, as taught in the prior art, will not provide the article of this invention. This invention is particularly useful for manufacturing shaped articles where temperature gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch, usually for joints at least 1 inch x at least 2 inches. Specifically, the importance of this step and of this invention is manifest in producing articles having as its smallest dimension 0.2 inch, i.e., at least 0.2 inch in thickness. It has been found that in such articles, the temperature gradients must still be controlled by the process of this invention in order to obtain the product of this invention.

Alternately, for steps 2 and 3, the pressure vessel can be used more efficiently by preheating polymer outside the reactor because heating polyethylene is a very slow process due to its high heat of fusion and its thermal insulation property. It can be heated in an oven, preferably in an inert atmosphere to prevent oxidation, particularly when the temperature is above 160°C. Because the UHMW polyethylenes do not flow when melted, they can be handled while hot and transferred to the preheated pressure vessel without deforming.

Product resulting from this modified process also is excellent for orthopedic replacement and has



certain superior characteristics. Values demonstrating these superior, enhanced qualities are shown in Example 11.

In addition to utility in the field of orthopedic replacement, the products prove useful in other applications also requiring the special properties of the products. Not only shaped articles are of interest, but also films and fibers as well as other "downstream" forms and unshaped granular forms of the product will prove useful. Film formed of the product of Example 5 is exemplified in Example 13. These examples are illustrative only, and other forms, shaped and unshaped, of the composition are contemplated within the scope of the invention. Therefore, "article" shall include both shaped articles and unshaped articles.

In a process more recently developed for manufacturing the product of this invention, the fluid used in the pressure vessel could be a gas that does not affect the UHMWLPE adversely. Specifically, the shaped article is formed from commercially available UHMWLPE. In the second step, the article is placed in a pressure vessel containing the fluid, in this case argon. However, it is necessary in the case where argon is used, to protect the UHMWLPE from any entry of the gas into the polymer by surrounding the article with a thin stainless steel or similar metal can as described in copending U.S. Patent Application (DE-0289C) filed to S. Li on November \_\_, 1989 which is a continuation-in-part of U.S. Serial No. 07/426,918 filed on October 24, 1989 which in turn is a continuation-in-part of U.S. Serial No. 07/288,576 filed December 22, 1988 which in turn is a continuation-in-part of U.S. Serial No. 07/278,912 filed on December 2, 1988. It should be understood

that other gaseous fluids may be used in place of argon. So long as the gas does not adversely affect  
5 or is prevented from adversely affecting the polymer and is not affected by the temperatures and pressures used in the process, the gas may be used.

In the next step, a pressure of at least 2800 ATM is applied and the vessel is heated to about  
10 220°C for about 6 hours. Thereafter, the temperature is "ramped" down at a rate no greater than about 10°C per hour to about 160°C while maintaining the pressure above 2800 ATM. The temperature is then  
15 "ramped" down at a maximum rate to 50°C while maintaining the high pressure, after which the pressure is released.

A further embodiment of the invention involves the following important steps:

1. forming by milling a casting or the like,  
20 the article from UHMWPE having a molecular weight of 400,000-10,000,000, preferably at least 1,000,000;

2. subjecting said article to a temperature of 190-340°C, preferably 320-340°C, for at least 0.5 hour, preferably at least one hour, in an inert  
25 atmosphere; and

3. cooling the article non-precipitously to a temperature of about 130°C or below. As in the other embodiments, the rate of cooling is such that temperature gradients in the shaped article are  
30 substantially avoided. Again, the rapid cooling sought in the prior art will not provide the article of this embodiment. The product of this non-pressurized embodiment is particularly useful for manufacturing shaped articles where temperature  
35 gradients pose a problem during the cooling step, i.e., where the article's cross-sectional dimensions are at least 1 inch x at least 1 inch, usually for joints at least 1 inch x at least 2 inches.

Specifically, the importance of this step and of this invention is manifest in producing articles having as  
5 its smallest dimension 0.2 inch, i.e., at least 0.2 inch in thickness.

For purposes of this invention, ultrahigh molecular weight linear polyethylene (UHMWLPE) is defined as a linear polyethylene having an estimated  
10 weight-average molecular weight in excess of about 400,000, usually 1,000,000 to 10,000,000 as defined by a melt index (ASTMD-1238) of essentially zero and a reduced specific viscosity (RSV) greater than 8, preferably 25-30. The relationships of RSV to  
15 intrinsic viscosity and to molecular weight are those developed by R. Chaing as presented by P. S. Francis et al. in J. Polymer Science, 31, 453 (1958).

It is envisioned that the modifications of adding a preliminary step heating the product to  
20 320-340°C will also provide superior characteristics to the product described by Li.

The improved properties of the products of this invention in its various embodiments are reflected in a tensile modulus of at least 300 kpsi, a flex  
25 modulus of at least 250 kpsi, ultimate tensile strength greater than 4000 psi, yield strength greater than 3500 psi and an elongation at break no greater than 500%.

A very important property of the product of  
30 this invention is its creep resistance. For prosthetic devices, e.g. knee, hip, elbow joints, etc., any substantial creep can be devastating in the loss of the benefits of extremely expensive surgery. Thus, the shaped articles of this invention display  
35 as little as a 0.5% loss in thickness when subjected to a compression pressure of 1000 psi for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621.

For some applications, still lower creep, higher stiffness, higher elongation, and particularly higher tensile strengths at yield are necessary. These can be introduced by the enhancing process if the polyethylene is first thermally heated at 320-340°C for thirty minutes or longer. The process depends on heating the polymer as near as possible to, without reaching, its decomposition point. The hot polymer should be cooled slowly because very rapid cooling, such as immersion in cold water, causes internal voids to form. This is caused by the combination of large volume changes polyethylene undergoes when melting (about 30%) and its poor heat conductivity. A convenient method is to allow the polymer to cool wrapped in insulation. The hot polyethylene can be put directly into the hot pressure vessel or it can be cooled and reheated to the normal 200°C in the pressure vessel.

The improved properties of the product of this part of the invention are reflected in tensile modulus of at least 350 kpsi, a tensile strength at yield of 3500-5400 psi, and a creep value of less than 0.6%.

In addition, the thermally heated polymer, still in the folded chain form used to make this superior form of this invention, in itself has improved elongation, crystallinity, and impact resistance over the starting material, but it is not equivalent to the enhanced form of polyethylene.

Perhaps the most characteristic property of the product of this invention is its infrared crystallinity index (IRCI). This property, which provides a reasonably accurate reflection of the crystallinity of this material, is in a range never before attained with any UHMW polyethylene materials. To determine this index, samples are

first obtained by microforming thin sections. Heat and pressure should be avoided during preparation of the samples. ICRI is the ratio of the band at 1894 reciprocal centimeters ( $\text{cm}^{-1}$ ) to the band at 1305 reciprocal centimeters ( $\text{cm}^{-1}$ ). Since the band at 1894  $\text{cm}^{-1}$  is attributed to the crystalline nature of the material and the band at 1305  $\text{cm}^{-1}$  is attributed to its amorphous nature, ICRI increases as the crystallinity increases. The product of this invention displays an IRCI of at least about 0.45. In fact, values of 0.73 and higher have been obtained. On the other hand, IRCI values for prior known UHMWLE's seldom reach above 0.3.

The invention will be more clearly understood by referring to the drawings and examples, which follow. In the drawings, Figure 1 is a schematic diagram of the equipment used in the process for forming the product of the invention using argon gas; and Figure 2 is a schematic diagram of the equipment used in the hydrostatic process.

In the examples, most of the properties are measured using standard ASTM tests.

All of the physical measurements were carried out under constant humidity (50% relative humidity) and temperature (23°C) conditions.

Tensile modulus, ultimate tensile strength, yield strength and elongation were measured according to ASTM D-638 with the following modifications:

- samples machined into shape without lubricating fluid
- type I tensile bar

- cross head speed = 0.2"/min for tensile modulus
- 2.0"/min for tensile stress and elongation.

Creep resistance was measured in accordance with ASTM D-621 with the following modifications:

- samples machined into cylinders or cubes without the use of lubricating fluids
- samples measured 0.5" x 0.5" x 0.5"

Flexural properties were measured according to  
15 ASTM D-790 with the following modifications:

- samples machined into shape without the use of lubricating fluids
- typical flex bar measures 0.125" thick x 0.5" width x 5" length
- span or gage is 2.0". (This was determined by a span/depth ratio of 16/1.)
- cross head speed = 0.05"/min (calculated based on span).

25            Impact resistance was measured using the  
notched Izod test given in ASTM D-256 with the  
following modifications:

- samples machined into shape without the use of lubricating fluid
- 30 • type A or notched IZOD
- specimen size is 0.5" x 2.5"
- 0.4" from bottom of vertex to opposite side
- 1.25" impacted end (from end of bar to vertex of notch)
- 35 • the notch should be the specified angle of 22.5 degrees.

It should be appreciated that in all  
5   embodiments of the invention the step of forming the  
     article by milling, casting, or the like from UHMWLPE  
     may be performed as the first step in the process  
     (i.e., before heating or preheating) or as the last  
     step in the process (i.e., after the cooling step).  
10       The following non-limiting examples, including  
     the improved and superior embodiments, illustrate the  
     basic principles and unique advantages of the present  
     invention. Various changes and modifications may be  
     made without departing from the spirit and scope of  
15   the present invention.

#### EXAMPLE 1

     The material used in this example is American  
     Hoechst Hostalen 415 GUR ultrahigh molecular weight  
20   polyethylene. It was obtained in the form of bars,  
     3" in diameter and up to 5' long in length. The  
     material will be referred to as UHMWLPE. The  
     molecular weight was over 1,000,000.

     One or more pieces of the UHMWLPE 11 were  
25   placed into stainless steel, seamless, 48" long  
     cylinders or sleeves 12. The thickness of the  
     stainless steel was 1/8". The bottom of the  
     cylinders was closed by welding a stainless steel cap  
     13 onto the bottom of the cylinder. The top of the  
30   cylinder was partially closed by welding on a  
     modified cap 14 which contained a vacuum port 15.  
     The cylinder was then evacuated using a vacuum pump  
     and sealed by crimping the port to form a can that  
     surrounds the piece of UHMWLPE completely. The  
35   sealed cylinder was then placed in a containment  
     vessel 16 large enough to hold 15 cylinders. The

containment vessel 16 was then placed into a hot isostatic pressing (HIP) unit 17 with molybdenum heating units 18. Thermocouples were added to monitor the temperature of the cylinders.

The basic function of the HIP process is to uniformly heat a load while applying pressure uniformly to all surfaces. The pressure medium used in this case was argon. The UHMWPE is protected from contact with the argon by the stainless steel cans.

The process conditions were:

1. Apply pressure to 39,000 psi.
2. Heat to 220°C.
3. Hold for 6 hours at 220°C and a minimum pressure of 41,000 psi (27 atmos.).
4. Ramp temperature down at a rate no faster than 10°C per hour to 160°C. Pressure is maintained above 41,000 psi during this time.
5. Ramp temperature down at maximum rate to 50°C while maintaining the pressure above 41,000 psi.
6. Below 50°C, pressure may be let down and the cycle ended.

The UHMWPE rods were then removed from the sleeves and parts were fabricated for physical testing. It is noted that the material produced exhibits much higher tensile modulus, flex modulus, melting point, density and creep resistance than the starting material (Control A).



15

	Material	DSC Melting Point (°C)	Density (grams/cc)	IRCI
5	Control	137.0-140.7°C	.93-.94	0.24
	Example 1	148.0-152.0°C	.947	≥ 0.45
	<u>ASTM D638</u>	<u>Control A</u>	<u>Example 1</u>	
10	Flex Modulus kpsi	165	291	
	Tensile Modulus kpsi	185	315	
	Ultimate Tensile kpsi	4500	4688	
15	<u>ASTM D638</u>			
	Yield kpsi	3476	4082	
20	Elongation (break) %	262	227	
	[values are averages of 5 tests]			

## ASTM D621 Creep Test

25	<u>Load</u>		
	500 psi	.5	.3 % deformation
	1000 psi	1.6	.7
	2000 psi	5.9	2.4

30

Additional evidence of the products' distinctiveness is found in data produced by small angle X-ray testing. A truly characteristic small-angle X-ray scattering plot of desmeared intensity (by the method of P. W. Schmidt, Acta Cryst., 13, 480 (1960) and Acta Cryst., 19, 938

35

(1965)) ( $I \times (2 \theta)^2$ ) versus scattering angle ( $2 \theta$ ) for the material of the invention exhibits two distinct scattering peaks associated with crystal long-spacings in the range of 480 angstroms (at  $2 \theta = .184$  degrees) and 4610 angstroms (at  $2 \theta = .0192$  degrees). The presence of the sharp diffraction peak at the lower angle is indicative of an extended polymer chain conformation (with a lamellar thickness greater than 2000 angstroms) whereas the more diffuse higher-angle peak corresponds to a lamellar thickness characteristic of conventional folded chain PE. This provides clear evidence for the presence of two scattering peaks in the subject invention material which correspond to lamellar thicknesses both above and below 2000 angstroms. By comparison, the previously patented extended chain polyethylene of Lupton et al., was reported to exhibit a complete absence of any detectable small angle X-ray scattering in the range of 50 to 2000 angstroms. Consequently this work demonstrates that the subject invention material is morphologically distinguishable from Lupton et al.

#### EXAMPLE 2

The material used in this example is an ultrahigh molecular weight polyethylene obtained from Jet Plastics, Inc.

A rod 21 measuring 6" x 1 1/8" was placed in the cavity 22 of a stainless steel, seamless, cylindrical reactor 23. The cavity 22 had a diameter of 1.35" and was about 9" long.

Water was fed into the cavity 22 at the entry port 24 through the use of a high pressure water pump

25 powered by compressed air. Simultaneously, the reactor was heated by electrical heaters 26  
5 surrounding the reactor.

In the first step, the rod 21 was heated to a temperature of 220°C under a hydrostatic pressure of 2000 ATM. The pressure was raised to 3000 ATM while the temperature was maintained at 220°C for 2 hours.  
10 The temperature was permitted to fall to 209°C over another 2 hour period, and then to about 182°C in 4 hours. Finally, the rod was cooled to 49°C by subjecting the reactor 23 to compressed air from the blower 27 over a period of one hour and the pressure  
15 released.

The rod was removed from the reactor and the surface was shaved. The product, a sample taken substantially from the center of the rod, displayed a DSC melting point of 154.5°C, and, on reheating, a  
20 DSC melting point of 140°C.

The material, when subjected to a compression pressure of 1000 psi for 24 hours at a temperature of 23°C and a relative humidity of 50% in accordance with ASTM D-621, deformed only 0.4%.

25 The other properties of the product were:  
flexural modulus - over 250 kpsi  
tensile modulus - over 300 kpsi  
tensile stress (yield) - over 3500 psi  
tensile stress (break) - over 4000 psi  
30 elongation (break) - less than 500%.

Its infrared crystallinity index was over 0.5.

The hydrostatic process described in Example 2  
35 is the best mode for preparing the product of this invention. This process has important advantages.

The pressure transfer liquid, water, is non-toxic and inexpensive. The hydraulic pressure is applied  
5 equally in all directions resulting in a substantially homogeneous product. This compares to processes shown in the prior art where hydraulic pressure is applied by a piston or a ram. In these  
10 latter cases, the high shrinkage polymer tends to solidify along the heat-escaping walls making it difficult for the pistons to advance and still apply the pressure uniformly. The result is a heterogeneous product.

It should be understood that although water is  
15 the preferred liquid fluid to use in the process, other liquids, with the same criteria as mentioned for gases, are also useful. Thus, methanol, ethanol, glycerin, glycols, etc. in addition to various aqueous solutions may be used.

20 The salt selected for an aqueous solution may be one that imparts a desirable property to the surface of the shaped article.

### EXAMPLE 3

25 This experiment was carried out in a manner similar to Example 2 except that the pressure in the first step was 3000 ATM. The material was maintained at 220°C under 3000 ATM for 4 hours. The temperature was allowed to fall to 190°C over an 8-hour period.  
30 After which, it was cooled to 100°C in 1 hour.

Samples were taken from 1/8" inside both ends of the rod and had melting points of 150.8°C and 153.2°C. When reheated, the melting points were 135.5°C and 138°C, respectively.

35 The infrared crystallinity index was 0.791; and the creep, when measured in accordance with ASTM

D-621, was less than 1%. These measurements were obtained on a sample taken from the center of the rod.

5

#### EXAMPLE 4

The experiment was also carried out in a manner similar to Example 2 except for the following changes in the heating/cooling cycle:

10           Heat at 211°C and 3000 ATM  
              and maintain for 1 hour;  
              Cool to 200°C in 1 hour at 3000 ATM;  
              Cool to 180°C over 5 hours at 3000 ATM  
              (cooling rate 200→180°C, 4°/hour); and  
15           Cool to 33°C in 1 hour and 3 minutes.

The product from inside both ends melted at 150°C and on reheating, at 135.5°C. The product, when tested in accordance with ASTM D-621 displayed a  
20           creep of less than 1%. Its infrared crystallinity index was 0.652.

#### EXAMPLE 5

A reactor with the general configuration shown  
25           in Figure 2 having an internal diameter of 4" and being 22" long, was charged with a 3 1/8" x 18 1/16" rod of UHMWPE (made from polymer from American Hoechst, Hostalen GUR 415). The closed vessel was evacuated, filled with water, and heated to 232°C at  
30           which point the pressure was increased to 3000 ATM with the water pump. This pressure was maintained until the end of the experiment. The reactor was held between 210 and 230°C for 3 hours, cooled over 1 hour to 200°C, cooled to 175°C in 5 hours (5°/hour)  
35           and then cooled to 80°C in 7 1/2 hours.

The resulting product rod was still in a cylindrical form with very little warpage. It measured 3 1/8" x 17 15/16". End pieces, 1/2" thick, were cut off each end of the rod revealing a uniform white color. Samples taken from the center of the rod on these cuts gave melting points of 152.9°C (201 J/g) and 152.1°C (207 J/g) when heated at 20°C/minute. When reheated, the melting points were 137.5°C.

A six inch section of the rod was sawed into 3/16" thick shapes for physical tests, then carefully milled to remove saw marks to 1/8" thickness. The resulting polymer had the following properties:

IZOD 18.7 ft. lb./in. of notch

Flexural Modulus 298.9 kpsi

Tensile Properties

Stress at yield 4190 psi

Stress (max.) 5430 psi  
(at break)

Elongation 280%  
(at break)

Modulus 378.3 kpsi

Creep Test, 0.6%

1000 psi

All tests at room temperature.

The crystallinity index (IRCI) was 0.528.

EXAMPLE 6

In this example, the product was prepared with  
5 an exceedingly smooth surface.

A polished brass disk, about 1 1/2" diameter,  
1/4" thick was pressed at 160°C against a UHMW  
polyethylene plug. The combination was cooled under  
pressure and sealed in a heat shrinkable Teflon FEP™  
10 tube. The polyethylene was converted in a  
hydrostatic system by this procedure in the vessel  
used in Example 5.

The heating, cooling cycle was as follows:  
3000 ATM and 210°C in 1 hour;  
15 3000 ATM 210°C to 200°C in 1 hour;  
3000 ATM 200°C to 178°C in 6 hours, 45 minutes;  
and  
3000 ATM 178°C to 23°C in 2 hours, 20 minutes.

20 The polyethylene did shrink so that it had a  
smaller diameter than the disk, but the polymer stuck  
to the surface. When forced apart, the surface was  
extremely smooth.

This technique is important in preparing  
25 complicated surfaces where smoothness is extremely  
important, such as on bearing surfaces such as  
medical prosthesis for knee and hip joints, or  
bearings for motor shafts, etc. Machine cutting  
polymers always leaves very small ridges.

30

EXAMPLE 7

The reactor of Figure 2, internal diameter 4"  
by 22" long was charged with a 3" x 18" rod of  
American Hoescht, Hostalen GUR 415 ultrahigh  
35 molecular weight polyethylene, water, and a nominal  
pressure of 100 psi. The system was heated to 170°C

to 176°C and held there for 1 hour, then the pressure was raised to 3000 ATM. The temperature was  
5 maintained at 179°C-174°C for 3 hours, during which time the polyethylene crystallized. The reactor was cooled to 79°C in 1.7 hours.

Two samples were taken; one from the center of the rod and another 1/2 inch from the outer surface  
10 of the rod. The melting points, as measured by DSC, were 150.9°C and 150.4°C, respectively, and upon reheating, 136.6°C and 137.3°C. Thus, the increases in melting points were 14.3°C and 12.7°C, respectively. The infrared crystallinity index was  
15 0.5.

#### EXAMPLE 8

This example shows that the polymer can be cooled at a rate as high as 34.5°C per hour in the  
20 critical cooling step (step 5) if proper precautions are taken to limit temperature gradients.

A one inch rod of UHMWLPE from Jet Plastics, Inc. was used. It was placed in the pressure vessel with water and subjected to the following treatments:  
25 3000 ATM and 220°C for 2 hours;  
3000 ATM, cool to 200°C in 50 minutes;  
3000 ATM, cool to 177°C in 40 minutes;  
3000 ATM, cool to 35°C in one hour.

30 A test sample taken one-half inch from the end of the rod and in the center displayed a DSC melting point of 153.8°C, and, on reheating a DSC melting point of 139.7°C.

The material, when subjected to a compression  
35 pressure of 1000 psi for 24 hours at 23°C and a relative humidity of 50% in accordance with ASTM D-621 deformed 0.5%.



EXAMPLE 9

Superior Enhanced UHMW Polyethylene prepared by  
 5 Preheating Polymer to 325°C.

A 3-1/16" x 15" rod of UHMW polyethylene  
 (Hoechst GUR415, fabricated by PolyHi) was heated to  
 325°C in an atmosphere of N<sub>2</sub> for six hours. The hot  
 rod was quickly placed in a pressure vessel preheated  
 10 to 212°C. The vessel was sealed immediately and  
 pressured with water to 3000 ATM. The cooling  
 schedule was as follows:

212° to 191°C 65 minutes  
 191° to 181°C 63 minutes  
 15 181° to 175°C 2 hours  
 175° to 174°C 6 hours, 26 minutes  
 174° to 45°C 3 hours, 15 minutes

The rod was cut into test samples and analyzed  
 with the following results:

20

DSC (Differential Scanning Calorimetry)

	<u>Center of Bar</u>	<u>1 cm from Bar Edge</u>
<u>m.p., °C</u>		
1st heat	150.5	152.4
25 2nd heat	137.9	139.0
ΔT	12.6	13.4

Heat of Fusion

1st heat 198.8 J/g  
 2nd heat 134.4 J/g

30 Infrared Crystallinity Index

(Samples cut from within 5 mm of bar edge)

In Bar Direction 0.613  
 Perpendicular to Bar Direction 0.633

Flex Modulus (KPSI)

35 424.0  
 386.1

<u>Deformation (Creep) ASTM D621 (% at 1000 psi load)</u>			
	In Bar Direction		0.4
5	Perpendicular to Bar Direction		0.6
<u>Density g/ml</u>			
	Gradient column		0.9595
	Infra Red		0.957, 0.958
10	<u>Tensile Properties:</u>		
	In Bar Direction	Perpendicular to	
	(6" Test Bars)	Bar Direction	
	(Type I)	(2-1/2" Test Bars)	
		(Type V)	
15	<u>Tensile Strength, PSI</u>		
	Yield:	4743	4516
		4758	4526
	Max:	4743	5614
20		4758	5005
	Break:	4396	5004
		3695	5040
	<u>Tensile Modulus,</u>		
	KPSI:	611.1	520.3
25		613.0	513.9
	<u>Elongation, %:</u>		
	Break	355	433
		315	400
	<u>IZOD IMPACT, ft.lb./in. of notch</u>		
30			Perpendicular to
	<u>Bar Direction</u>	<u>Bar Direction</u>	
	24.8	26.1	
	22.0	25.0	
35			

EXAMPLE 10

Effect of Sequence of Heat-treatment, Cooling,  
 5 Reheating to a Lower Temperature, and Pressure  
 Recrystallization on UHMWPE.

A UHMW PE bar (3" x 15") of the same type as in  
 Example 1 was heated for five hours at 325°C under  
 N<sub>2</sub>, then slowly cooled to room temperature. It was  
 10 reheated to 225°C, and pressure recrystallized as  
 described in Example 9 according to the following  
 schedule:

	241° to 191°C	3000 ATM	2 hours, 15 minutes
	191° to 181°C	3000 ATM	2 hours
15	181° to 171°C	3000 ATM	6 hours

The resulting product was machined into test  
 pieces and analyzed with the following results:

DSC

	<u>Center of Bar</u>	<u>1 cm in from Bar Edge</u>
20		
	<u>m.p., °C</u>	
	1st heat	149.3
	2nd heat	134.3
	ΔT	15

25 Heat of Fusion

	1st heat	223.6 J/g	229.6 J/g
	2nd heat	156.1 J/g	162.3 J/g

Infrared Crystallinity Index

	In Bar Direction	0.745
30	Perpendicular to Bar Direction	0.759

Tensile Properties

## Tensile Strength, PSI

	At Yield	4706	4463
	At Break	5362	5326

26

	Tensile Modulus,		
	KPSI:	649.7	404.2
5	Elongation, %		
	At Yield	4.7	4.5
	At Break	330	335
	Deformation (Creep) ASTM D621 Test		
	(% at 1000 psi load)		
10		0.4	
		0.3	

#### Effect of Preheating by Reflux

Alternatively, the preliminary heating of  
 15 Example 10 may be achieved by refluxing in vapors as described below.

A 3" x 18" rod of UHMWLPE (American Hoechst, Hostalen GUR 415) was heated in refluxing vapors of Krytox®-143AZ (E. I. du Pont de Nemours and Company,  
 20 Wilmington, Delaware) (at 333-335°C) for 2 hours, 40 minutes. Krytox®-143AZ is a perfluoroalkylpolyether that is a nonflammable, chemically inert liquid having unusually high thermal and oxidative stability. Other materials demonstrating these  
 25 characteristics may also be suitable. The system was protected by a nitrogen atmosphere and was wrapped with glass insulation to facilitate slow cooling. As compared to the starting material, the resulting product has improved crystallinity (IRCI from 0.27 to  
 30 0.47), a tensile modulus (from 210 KPSI to 300 KPSI), and tensile strength at yield (from 3400 to 3850 psi). Most significantly, the product displays a large increase in elongation at break (from 315% to 893%).

35

When the above described material was recrystallized from 220°C under 3000 ATM, a new polyethylene resulted possessing extremely high elongation at break (667%) along with the high tensile strength at yield (4900 psi) and the tensile modulus (574 KPSI) expected of the superior, enhanced UHMWLPE materials.

10	Flex Modulus, KPSI	436.4
		431.2
		433.80 (av)
	Density	.9684
	IZOD IMPACT,	
15	(ft.lb./in. of notch)	17.1
		15.9
		16.5 (av)

#### EXAMPLE 11

Further evidence shows that UHMWPE polymer pretreated to at least 325°C gives a superior enhanced material (SEUHMW PE).

The purpose of this Example is to show the importance of the preheat temperature.

25	Preheat Temperature(C°C)	225	290	310	325
	Crystallinity Index	.553	.550	.605	0.76
	Heat of Fusion, J/g	186	200	190	219
	Tensile, Yield PSI	4268	4277	4212	4819
30	Deformation (Creep)				
	ASTM D621 Test				
	(% at 1000 psi load)	0.6			0.4
	IZOD ft.lb./in.				
	of Notch	20.6	20.7	20.6	24
35					

Effect of Heating Temperature on UHMW PE

The samples were heated by placing 3/4" cubes of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabricated by Westlake) wrapped in Teflon® film in a large test tube protected from air with N<sub>2</sub>. In the first experiment, a small thermocouple was inserted into the center of the cube, the purpose being to determine the time necessary for the sample to reach test temperature. A plug of glass wool was placed above the sample to control convection currents. The tube was heated with a Wood's metal bath. After the heat treatment was complete, the sample was wrapped in insulation to ensure slow cooling. At a bath temperature of 250°C, the sample required 45 minutes to reach test temperature.

20	Time Sample at Temperature <u>hrs:min</u>	Test Temperature <u>°C</u>	Crystallinity Index <u>(by IR)</u>
	4:00	250	0.232
	20:00	250	0.244
25	4:00	293	0.264
	:01	293	0.230
	4:00*	320-325	0.374
	1:00*	334-335	0.378
	1:00*	340-342	0.391

30

\*Heated by submerging sample wrapped in Teflon® film under Woods metal as described in the following paragraph.

35

Effect of Time on Heating UHMW PE

Small cubes (3/4") of UHMW PE cut from the rod form of Hoechst Hostalen GUR 415 were wrapped in Teflon® film, tied to a glass rod, and pushed under the surface of a Wood's metal bath. In the first experiment, a small thermocouple was inserted in the cube. When plunged into a 322-329°C bath, twelve minutes were required for the sample center to reach 321°C. The time at temperature (not the time in the bath) is recorded below. The samples were removed from the bath and wrapped in glass fiber insulation to permit slow cooling which required 1.5 hours to reach 80°C. The extent of change was determined by measuring crystallinity indices.

	Time Sample	Crystallinity
	(at 320-325°C <u>(hrs:min)</u> )	<u>Index by (IR)</u>
20	no heating	.258
	0:10	.261
	0:20	.294
	1:00	.330
	4:00	.374

25

Heat Treatment of UHMW PE (Large Scale)

A 3" diameter by 18" bar of UHMW polyethylene (Hoechst Hostalen GUR 415, m.w. 4-6 million, fabrication by Westlake) was heated under nitrogen at 325°C for 4 hours (65B). The bar was cut into test pieces as was a bar of the same starting polymer that had not been treated. Tests were run sequentially.

35

30

		Untreated <u>Polymer</u>	Thermally <u>Treated</u>	% <u>Difference</u>
5	<u>DSC</u>		sharper (narrow curve)	
	m.p. °C	139.7	137.5	
	Heat of Fusion J/g	154.6	197.5	+28
10	Crystallinity Index (IR)	0.258	0.386	+50
	<u>Tensile Properties</u>			
	Tensile Strength, psi			
	Yield	3380	3694	
15		3456	3642	
		3418 (av)	3668 (av)	+7.3
	Max.	5361	4706	
		4864	4673	
		5113 (av)	4690 (av)	
20	Break	5361	4705	
		4864	4673	
		5113 (av)	4689 (av)	
	Elongation, % Break			
		330	490	
25		300	500	
		315 (av)	495 (av)	+57
	Modulus, KPsi	208.4	244.6	
		210.5	253.7	
		209.5 (av)	249.1 (av)	+19
30	Flex Modulus, KPsi			
		124.4	151.5	
		137.1	146.8	
		130.7 (av)	149.1 (av)	+14
	IZOD IMPACT, (ft.lb./in. of notch)			
35		15.93	19.97	
		20.81	22.68	
		18.37 (av)	21.32 (av)	+16



Deformation (Creep) ASTM D621 Test  
(% at 1000 psi load)

5	1.8	1.6	-17
	1.7	1.3	

Similarly, a 3" diameter bar of different UHMW polyethylene (Himont 1900, m.w. 1,000,000) was heat pretreated in an inert atmosphere, for example, of N<sub>2</sub>. The physical properties of the product had greatly improved elongation and impact resistance.

		Untreated <u>Polymer</u>	Thermally <u>Treated</u>	% <u>Difference</u>
15	<u>DSC</u>			
	Heat of			
	Fusion J/g	166.3	190.7	+15
	Crystallinity			
	Index (IR)	.284	.379	+33
20	<u>Tensile Properties</u>			
	Tensile Strength, psi			
	Yield	3544	3721	
		3703	3589	
		3622 (av)	3655 (av)	- 0
25	Max.	7387	6545	
		7190	5999	
		7289 (av)	6272 (av)	-14
	Elongation, % Break			
30		200	343	
		216	293	
		208 (av)	318 (av)	+53
	% Yield	16.6	20	
		20	16.6	
35	Modulus, KPsi	128.4	212.7	
		216.2	192.7	
		202.7 (av)	202.7 (av)	0

IZOD IMPACT, (ft.lb./in. of notch)

	13.05	24.26	
5	11.94	17.12	
	12.49 (av)	21.09 (av)	+65

#### EXAMPLE 12

10 A 3" diameter bar (rod), 18" in length, of  
American Hoechst Hostalen GUR 415 ultrahigh molecular  
weight polyethylene, was heated in an oven and then  
encapsulated with low molecular weight polyethylene  
by rolling the hot rod onto a 1/16" sheet of low  
molecular weight polyethylene heated to 180°C on a  
15 large hot plate. An intervening sheet of "Teflon"  
Polytetrafluoroethylene film was kept on the  
encapsulated rod to prevent sticking to the hot  
plate. The rod ends were similarly sealed. The  
"Teflon" film was kept on the encapsulated rod to  
20 prevent sticking in the reactor.

The bar was heated to 225°C under a nitrogen  
atmosphere and transferred to the reactor at 225°C.  
After sealing, the reactor pressure was taken to 3000  
atmospheres which caused the temperature to reach  
25 237°C. The reactor was permitted to cool to 180°C in  
6.5 h, then maintained at this temperature for 1h.  
The temperature was dropped to 170°C, held at this  
temperature for 3h, then cooled slowly to 150°C from  
where it was cooled rapidly.

30 The rod, which remained coated, was cut and  
machined into two test pieces (A and B) which gave  
the following results:

		<u>SAMPLE</u>	
<u>DSC</u>		<u>A</u>	<u>B</u>
5	<u>1st Heat:</u>		
	Melt point, °C	149.1	153.7
	Heat of Fusion, J/g	219.8	209.5
	<u>2nd heat:</u>		
	Melt point, °C	135.5	136.6
10	Heat of fusion, J/g	141.2	144.9
	<u>Crystallinity Index (IR)</u>	0.566	0.567
	<u>Tensile Properties:</u>		
	Tensile Strength, psi		
	At Yield	4149	4076
15	At Max.	7448	8138
	At Break	7448	8138
	Elongation, %	323	346
	Modulus, Kpsi	363.6	358.2
	Creep Deformation, % (D621)	0.6	0.6
20	IZOD Impact,	15.9	15.8
	(ftlb/in. of notch)		

EXAMPLE 13

A 5.75" segment of enhanced ultrahigh molecular weight polyethylene prepared as in Example 5, was skived to two films (A and B), of 11 mil and 5 mil thickness, respectively. The following properties were obtained (averaged from five tests per film sample):

30		<u>SAMPLE</u>	
		<u>A</u>	<u>B</u>
	<u>Tensile Properties:</u>		
	Tensile Strength, psi		
	At Yield	3035	3108
35	At Max.	6554	4083
	At Break	6481	4083
	At 5% Elongation	2667	2705

34

Tensile Modulus, Kpsi	129.7	165.6
Elongation at Break, %	470	237.6

5

The skived films were hot drawn in a tenter frame at 140°C. One piece of the 5 mil film was drawn 6 fold in one direction (C). A second piece of the 5 mil film was drawn 3 fold in both directions (D):

10

SAMPLECD

Tensile Strength, psi:

15	At Yield	37,819	13,720
	At Max.	42,058	19,358
	At Break	46,426	18,995
	Tensile Modulus, Kpsi	93.3	94.9
	Elongation at Break, %	56	132.4
20	Thickness, mils	2.6	1.6

CONTROL B

In this experiment, a product was prepared in the manner of Example 1 of U.S. Patent No. 3,944,536.

25 A sample of the ultrahigh molecular weight polyethylene used in Example 1 previously described herein, measuring 1/4" x 1/4" x 1/8" thick was heated between a film of polytetrafluoroethylene on a hot plate at atmospheric pressure and at a temperature of 30 160°C on the upper side and 270°C on the lower side.

The molten sample was transferred quickly to a hydraulic press at room temperature where the sample was subjected to a pressure of 8 tons (about 250,000 psi or about 16,000 ATM). It required 1.6 seconds to 35 attain full pressure. The resulting polymer was

35

tested. It displayed an infrared crystallinity index  
of 0.199. Its melting point was 134.5°C and, when  
5 reheated, 134.4°C.

10

15

20

25

30

35

CLAIMS

What is claimed is:

5

1. An ultrahigh molecular weight linear polyethylene exhibiting a flexural modulus of 250,000-500,000 psi, a tensile stress at yield of 3500-4500 psi, a tensile stress at break of 4000-9000  
10 psi, a tensile modulus of 300,000-700,000 psi, a notched Izod impact resistance of 12-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 1% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene  
15 having a molecular weight of 400,000-10,000,000, a single crystalline melting point of greater than 144°C, the reduction in said melting point upon reheating being greater than 11°C and an infrared crystallinity index of at least about 0.45.

20

2. The composition of Claim 1 wherein the tensile modulus is 300,000-600,000 psi, the notched Izod impact resistance is 12-20 ft. lb. per inch of notch and the infrared crystallinity index is at  
25 least 0.5.

30

3. The composition of Claim 2 shaped into an article wherein its dimensions are at least one inch by at least one inch.

4. The composition of Claim 2 shaped into an article wherein its smallest dimension is at least 0.2 inch.

35

5. The composition of Claim 2 wherein its infrared crystallinity index is at least about 0.5.

6. An article consisting essentially of the  
5 ultrahigh molecular weight linear polyethylene of  
Claim 1 exhibiting a flexural modulus of  
250,000-500,000 psi, a tensile stress at yield of  
3500-4500 psi, a tensile stress at break of 4000-9000  
psi, a tensile modulus of 300,000-700,000 psi, a  
10 notched Izod impact resistance of 12-25 ft. lb. per  
inch of notch, a creep at a compression of 1000 psi  
of less than 1% after 24 hours at a temperature of  
23°C and a relative humidity of 50%, the polyethylene  
having a molecular weight of 400,000-10,000,000, a  
15 single crystalline melting point of greater than  
144°C, the reduction in said melting point upon  
reheating being greater than 11°C and an infrared  
crystallinity index of at least about 0.45.

20 7. The shaped article of Claim 6 wherein the  
tensile modulus is 300,000-600,000 psi, the notched  
Izod impact resistance is 12-20 ft. lb. per inch of  
notch and the infrared crystallinity index is at  
least 0.5.

25 8. The shaped article of Claim 6 wherein its  
dimensions are at least one inch by at least one inch.

9. The shaped article of Claim 6 wherein its  
30 smallest dimension is at least 0.2 inch.

10. The shaped article of Claim 6 wherein its  
infrared crystallinity index is at least about 0.5.

35 11. A process for obtaining the ultrahigh  
molecular weight linear polyethylene of Claim 1  
consisting essentially of the following steps:

(a) forming said article of an ultrahigh  
molecular weight linear polyethylene having a  
5 molecular weight of 400,000-10,000,000;

(b) subjecting said article to a fluid  
under pressure of at least 2800 ATM and a temperature  
of 190°C-300°C;

(c) maintaining the temperature from  
10 190°C-300°C and the pressure of at least 2800 ATM for  
at least 0.5 hour;

(d) reducing the temperature to at least  
below 160°C-170°C while maintaining the pressure at  
at least 2800 ATM, the rate of reduction in  
15 temperature being such that temperature gradients in  
the shaped article are substantially avoided; and

(e) cooling to a temperature of about  
130°C or below and releasing the pressure to  
approximately 1 ATM in a manner such that remelting  
20 of said article is prevented.

12. The process of Claim 11 wherein step (a)  
is performed after step (e) is performed.

25 13. The process of Claim 11 wherein said  
fluid is water.

14. The process of Claim 13 wherein said  
pressure in step (b) is at least 3000 ATM.  
30

15. The process of Claim 13 wherein said  
temperature in step (b) is 200°C-230°C.

16. The process of Claim 13 wherein the  
35 temperature and pressure in step (e) is maintained  
for at least one hour.



17. The process of Claim 13 wherein the  
5 surface of the article is shaved after step (e).

18. The process of Claim 13 wherein the  
cooling rate in step (d) is no greater than 35°C per  
hour.

10

19. The process as in Claim 13 wherein the  
cooling rate in step (d) is no greater than 10°C per  
hour.

15

20. An ultrahigh molecular weight linear  
polyethylene exhibiting a flexural modulus of  
250,000-650,000 psi, a tensile stress at yield of  
3500-5400 psi, a tensile stress at break of 4000-6000  
psi, a tensile modulus of 300,000-700,000 psi, a  
20 notched Izod impact resistance of 12-25 ft. lb. per  
inch of notch, a creep at a compression of 1000 psi  
of less than 1% after 24 hours at a temperature of  
23°C and a relative humidity of 50%, the polyethylene  
having a molecular weight of 400,000-10,000,000, a  
25 single crystalline melting point of greater than  
144°C, the reduction in said melting point upon  
reheating being greater than 11°C and an infrared  
crystallinity index of at least about 0.45.

30

21. The composition of Claim 20 wherein the  
tensile modulus is 300,000-650,000 psi, the notched  
Izod impact resistance is 12-25 ft. lb. per inch of  
notch and the infrared crystallinity index is at  
least 0.5.

35

22. The composition of Claim 21 shaped into  
an article wherein its dimensions are at least one  
5 inch by at least one inch.

23. The composition of Claim 21 shaped into  
an article wherein its smallest dimension is at least  
0.2 inch.

10

24. The composition of Claim 21 wherein its  
infrared crystallinity index is at least about 0.5.

25. An article consisting essentially of the  
15 ultrahigh molecular weight linear polyethylene of  
Claim 20 exhibiting a flexural modulus of  
250,000-650,000 psi, a tensile stress at yield of  
3500-5400 psi, a tensile stress at break of 4000-6000  
psi, a tensile modulus of 300,000-700,000 psi, a  
20 notched Izod impact resistance of 12-25 ft. lb. per  
inch of notch, a creep at a compression of 1000 psi  
of less than 1% after 24 hours at a temperature of  
23°C and a relative humidity of 50%, the polyethylene  
having a molecular weight of 400,000-10,000,000, a  
25 single crystalline melting point of greater than  
144°C, the reduction in said melting point upon  
reheating being greater than 11°C and an infrared  
crystallinity index of at least about 0.45.

30 26. The article of Claim 25 wherein the  
tensile modulus is 300,000-650,000 psi, the notched  
Izod impact resistance is 12-25 ft. lb. per inch of  
notch and the infrared crystallinity index is at  
least 0.5.

35

27. The article of Claim 26 wherein its dimensions are at least one inch by at least one inch.

5

28. The article of Claim 26 wherein its smallest dimension is at least 0.2 inch.

29. The article of Claim 25 wherein its infrared crystallinity index is at least about 0.5.

10

30. A process for obtaining the article of Claim 25 consisting essentially of the following steps:

15

(a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;

(b) subjecting said article to a preliminary heat treatment at a temperature of between 320-340°C, in an inert atmosphere for at least 0.5 hour;

20

(c) subjecting said article to a fluid under pressure of at least 2800 ATM and a temperature of 190°C-300°C;

25

(d) maintaining the temperature from 190°C-300°C and the pressure of at least 2800 ATM for at least 0.5 hour;

30

(e) reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM, the rate of reduction in temperature being such that temperature gradients in the shaped article are substantially avoided; and

35

(f) cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting of said article is prevented.

31. The process of Claim 30 wherein step (a)  
5 is performed after step (f) is performed.

32. The process of Claim 30 wherein said  
fluid is water.

10 33. The process of Claim 32 wherein said  
pressure in step (c) is at least 3000 ATM.

34. The process of Claim 32 wherein said  
15 temperature in step (c) is 200°C-230°C.

35. The process of Claim 32 wherein the  
temperature and pressure in step (f) is maintained  
for at least one hour.

20 36. The process of Claim 32 wherein the  
surface of the article is shaved after step (f).

37. The process of Claim 32 wherein the  
25 cooling rate in step (e) is no greater than 35°C per  
hour.

38. The process as in Claim 32 wherein the  
cooling rate in step (e) is no greater than 10°C per  
hour.

30 39. An improved folded chain ultrahigh  
molecular weight linear polyethylene exhibiting a  
flexural modulus of 150,000-300,000 psi, a tensile  
stress at yield of 3500-4000 psi, a tensile stress at  
35 break of 4000-6000 psi, a tensile modulus of  
150,000-300,000 psi, a notched Izod impact resistance

of 15-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 2% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, preferably of at least 1,000,000 and an infrared crystallinity index of at least about 0.35.

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40. The composition of Claim 39 wherein the elongation (% at break) is 250-900, the notched Izod impact resistance is 15-20 ft. lb. per inch of notch.

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41. The composition of Claim 39 shaped into an article wherein its dimensions are at least one inch by at least one inch.

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42. The composition of Claim 39 shaped into an article wherein its smallest dimension is at least 0.2 inch.

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43. An article consisting essentially of the improved folded chain ultrahigh molecular weight linear polyethylene of Claim 39 exhibiting a flexural modulus of 150,000-300,000 psi, a tensile stress at yield of 3500-4000 psi, a tensile stress at break of 4000-6000 psi, a tensile modulus of 150,000-300,000 psi, a notched Izod impact resistance of 15-25 ft. lb. per inch of notch, a creep at a compression of 1000 psi of less than 2% after 24 hours at a temperature of 23°C and a relative humidity of 50%, the polyethylene having a molecular weight of 400,000-10,000,000, preferably of at least 1,000,000 and an infrared crystallinity index of at least about 0.35.

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44. The article of Claim 43 wherein the elongation (% at break) is 250-900, the notched Izod impact resistance is 15-20 ft. lb. per inch of notch.

45. The article of Claim 44 wherein its dimensions are at least one inch by at least one inch.

46. The article of Claim 44 wherein its smallest dimension is at least 0.2 inch.

47. A process for obtaining the article of Claim 43 consisting essentially of the following steps:

(a) forming said article of an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000-10,000,000;

(b) subjecting said article to a temperature of 190°C-340°C for at least 0.5 hour in an inert atmosphere; and

(c) cooling the article non-precipitously to a temperature of about 130°C or below.

48. The process of Claim 47 wherein step (a) is performed after step (c) is performed.

49. The process of Claim 47 wherein said temperature in step (b) is 320°C-340°C.

50. The process of Claim 47 wherein the temperature in step (b) is maintained for at least one hour.

51. A process for producing a superior, enhanced ultrahigh molecular weight polyethylene

displaying an elongation at break of at least 400% consisting essentially of the following steps:

- 5           (a)     subjecting an ultrahigh molecular weight linear polyethylene having a molecular weight of 400,000 to 10,000,000 to a preliminary heat treatment of refluxing vapors at a temperature of between 320-340°C, in an inert atmosphere for at  
10   least 0.5 hour;
- (b)     subjecting said article to a fluid under pressure of at least 2800 ATM and a temperature of 190°C-300°C;
- (c)     maintaining the temperature from  
15   190°C-300°C and the pressure of at least 2800 ATM for at least 0.5 hour;
- (d)     reducing the temperature to at least below 160°C-170°C while maintaining the pressure at at least 2800 ATM, the rate of reduction in  
20   temperature being such that temperature gradients in the shaped article are substantially avoided; and
- (e)     cooling to a temperature of about 130°C or below and releasing the pressure to approximately 1 ATM in a manner such that remelting  
25   of said article is prevented.

52.    The process of Claim 51 wherein said fluid is water.

30       53.    The process of Claim 51 wherein said pressure in step (b) is at least 3000 ATM.

54.    The process of Claim 51 wherein said temperature in step (b) is 200°C-230°C.

5 55. The process of Claim 51 wherein the  
temperature and pressure in step (e) is maintained  
for at least one hour.

10 56. The process of Claim 51 wherein the  
surface of the article is shaved after step (e).

57. The process of Claim 51 wherein the  
cooling rate in step (d) is no greater than 35°C per  
hour.

15 58. The process as in Claim 51 wherein the  
cooling rate in step (d) is no greater than 10°C per  
hour.

20 59. The product produced by the process of  
Claim 51.

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# INTERNATIONAL SEARCH REPORT

International Application No **PCT/US 89/05261**

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup>: A 61 L 27/00, A 61 F 2/32, C 08 L 23/06

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System

Classification Symbols

IPC<sup>5</sup>

A 61 L, A 61 F, C 08 L

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	Polymer, volume 22, January 1981, IPC Business Press, (London, GB) , S.K. Bhateja: "Unaxial tensile creep behaviour of ultra high molecular weight linear polyethylene", pages 23-28, see page 28, conclusions --	1
A	Journal of Polymer Science: Part A2, Polymer Physics, volume 7, 1969, John Wiley & Sons, (New York, US) T.D. Davidson et al.: "Extended-chain Crystals. II. Crystallization of polyethylene under elevated pressure", pages 2051-2059, see page 2052, lines 32-38  -----	1

<sup>10</sup> Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

29th March 1990

Date of Mailing of this International Search Report

**03 MAY 1990**

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

*[Signature]*  
MISS T. TAVERNA